SIMULATION OF HETEROGENOUSLY CATALYZED ESTERIFICATION FOR THE PRODUCTION OF BIODIESEL USING REACTIVE DISTILLATION COLUMN

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I declare that this thesis entitled “simulation of heterogenously catalyzed esterification for the production of biodiesel using reactive distillation column ” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

Signature :……..

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Date : 30 April 2009

Special Dedication to my mother, Rus Binti Omar and
my father Dr. Hasan Bin Bahrom,my brothers and sister and
all my family members,my girlfriend Fatimawati Binti Mat Isa
my friends, my fellow colleague and all faculty members

For all your care, support and believe in me, Thank You.

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ABSTRACT

Fatty acid esters serve as feedstock for production of cosmetic, detergents, and as a fuel for production of biodiesel. They were produced by the reaction between fatty acids and the alcohols to produced fatty acid ester and water. The reactive distillation column performance for the production of 2-ethylhexyl dodecanoate by esterification of dodecanoic acid with 2-ethylhexanol has been studied in present research. Simulation on esterification process was done in equilibrium stage model using RADFRAC model. Kinetic model and thermodynamic model based on concentration is incorporate into RD equilibrium stage model. The simulation was carried out to determine the effect of the important parameter and design factor such as column operating pressure, reflux ratio, feed location arrangement, height of reactive zone and also the temperature of reactant feed enters to the column. A technically optimized RD process for production of 2-ethylhexyl dodecanoate has been proposed based on the simulated data. As a result, the optimum operating parameters are, reflux ratio at 0.1, temperature of feed enters to the column both are at 303.15 right on the reactive zone at stage five and stage 10, Height of reactive zone is six stages, whereby the operating column pressure is 30kpa in order to have an acid conversion about 99.3%.

ABSTRAK

Ester asid lemak digunakan sebagai bahan mentah untuk penghasilan kosmetik, detergen dan bahan api untuk penghasilan biodiesel. Ianya dihasilkan melalui tindak balas antara asid lemak dan alkohol untuk menghasilkan ester asid lemak dan air. Perlaksanaan kolum penyulingan reaktif untuk penghasilan 2-ethylhexyl dodecanoate melalui proses esterifikasi dodecanoic acid dengan 2-ethylhexanol telah dikaji ketika ini. Simulasi terhadap proses esterifikasi telah dilakukan pada model tahap persamaan menggunakan RADFRAC model. Model kinetic dan thermodinamik berdasarkan kepekatan digabungkan kepada model tahap persamaan RD. Simulasi yang dilakukan adalah untuk mengenal pasti kesan parameter yang penting dan faktor reka bentuk seperti tekanan operasi kolum, kadar refluk, susunan lokasi bahan kemasukan, ketinggian zon reaktif dan juga suhu bahan tindak balas yang masuk kedalam kolum. Secara teknikal, pengoptimaan proses RD untuk penghasilan 2-ethylhexyl dodecanoate telah dicadangkan berdasarkan kepada data yang disimulasi. Keputusannya, parameter operasi yang optima adalah, kadar reflux 0.1, suhu bahan tindak balas yang masuk kedalam kolum adalah 303.15 pada zon reaktif pada peringkat ke lima dan peringkatan, ketinggian zon reaktif ialah enam peringkat, di mana tekanan operasi kolum adalah 30kPa untuk mendapatkan penukaran asid sehingga mencapai 99.3%.

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E_a	activation energy, kJ mol^{-1}
K_c	rate constant for catalysed reactio, m^6 s^{-1} $mol^{-1}kg^{-1}$
K_u	rate constant for non-catalysed reactio, m^6 s^{-1} $mol^{-1}kg^{-1}$
K_x	activity-based reaction equilibrium constant
P	pressure, kPa
r	reaction rate per unit volume, mol $s^{-1}m^{-3}$
T	temperature, K

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Fatty acid esters serve as feedstock for production of cosmetic, detergents, and surfactant and as a fuel for production of biodiesel. They were produced by the reaction between fatty acids and the alcohols to produced fatty acid ester and water. Fatty acid or derivatives fatty acid are used in a wide varieties of applications. The demands of fatty acid are even increasing for the past 10 years. Fatty acids are typically present in the raw material used for production of biodiesel. Esterifications, transesterifications and etherifications are the reaction to produced fatty acid ester. Transesterification reaction of triolein with alcohol for a production of biodiesel carried out by (Tanguy F. Dossin et al., 2006) to produce methyl oleate from rapeseed oil and also the direct esterification of fatty acid with alcohol and catalyzed by acid catalyzed as homogenously (F. Omota et al., 2003)

Since biodiesel has become increasingly attractive because it is made from renewable sources and combines high performance with environmental benefits. The idea of using vegetable oil as fuel for diesel engines is over a century old. In fact, Rudolph Diesel himself demonstrated the performances of his engine using peanut oil as fuel. Unlike petroleum diesel that contains hydrocarbons, biodiesel consists of a mixture of monoalkyl esters of long-chain fatty acids. These are typically produced by (Trans) esterification. Biodiesel has several advantages over petroleum diesel: it is safe, renewable, nontoxic, and biodegradable; it contains no sulfur and is a better

lubricant. The investigations for esterification reactions also have been carried out. They are and heterogeneously catalyzed using solid catalyst such as zinc acetate (Bhatia et al., 2006), Amberlyst 15 (Guido et al. 2006), magnesium oxide (Tanguy, 2006). However there are problem occur in this homogenously catalyzed process whereby it requires neutralization and separation from the reaction mixture, leading to a series of environmental problem that related to large amounts of solvent and energy.

Because of homogenous problem, heterogeneously catalyzed esterification process is presented. This is because esterification of alkyl ester can be easily separated from the reaction mixture without requiring the use of a solvent, show easily regeneration and have less corrosive character that leading to safer, cheaper, and more environmental-friendly operation. In addition heterogeneously catalyzed reactive distillation offers advantages over the homogenously catalyzed process alternative e.g. sulfuric acid. Size and location of the reactive section can be chosen regardless of the thermodynamic constrain and at the same time corrosion problem will be minimized. Furthermore, the separation of the homogenous catalyst from the product (ester) that is obtained as bottom product can be avoided.

Esterification of heterogeneously catalyzed in fact brings to the used of reactive distillation column (RD). Reactive distillation column has become an interesting alternative to some conventional process processes, especially for equilibrium-limited reaction as esterification and etherification. RD is cheapest method than the traditional method that consists of reactor followed by trains of distillation column shows in the flow sheet; see figure 1.1.

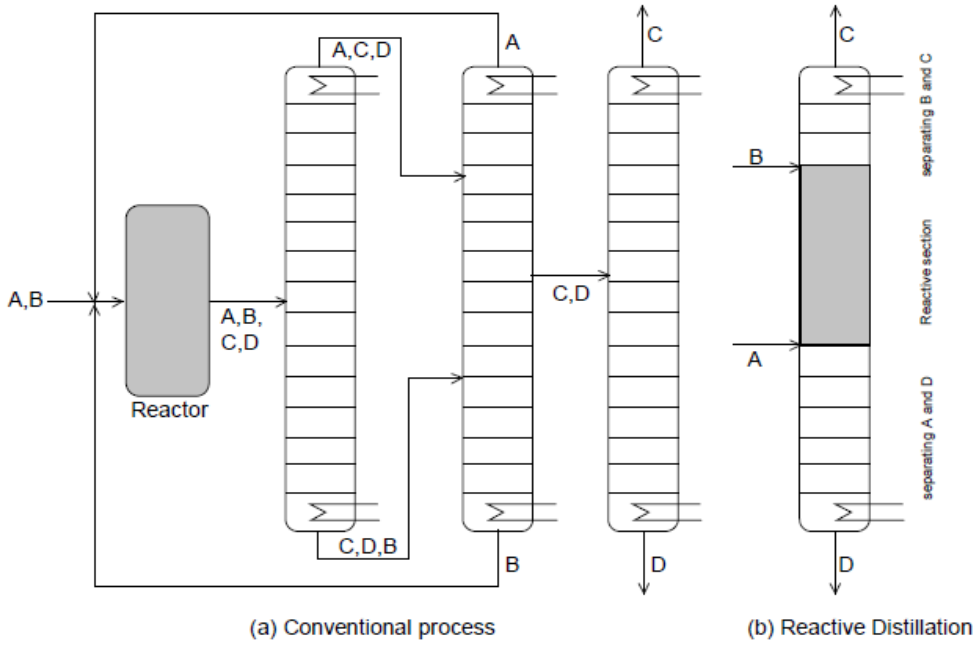

Figure 1.1: Processing scheme for processing A and B to produce C and D where (a) typical configuration of a conventional process consisting of a reactor followed by a distillation train (b) the reactive distillation configuration

The reactive distillation is featured with merits not only in reducing both capital and operational cost as its multifunctional nature, but also in promoting the reaction conversion. Not only that, the commercial success of RD for production of methyl tert-butyl ether (MTBE) and methyl acetate demonstrate its ability to render cost-effectiveness and compactness to the chemical plant (Sharma & Mahajani, 2003). So, as a consequence, RD has been explored as potentially alternative for several chemical production and reactions.

1.2 Problem statement

The needs and demands for fuel has been sky rocketing for the past years as a result to increment price of world's crude oil. Fossil fuel that has been the major contributor to global economy is unsustainable but yet the demand for the energy is increasing year by year, as well as increases of environmental and human health

impact. This contributes to the high productions of biodiesel fuel as an alternative fuel that costless and environmentally harmless. However, the combination of reaction and distillation within one unit operation is called reactive distillation can contribute to costless operation while producing these demands. The direct removal of the products or intermediates results in higher conversions and selectivity in comparison with the classical, sequential approach.

In recent years RD have been used as one of the important simultaneous implementation of reaction separation within a single unit of column. It also been used as a production of biodiesel. The natural multiple function of RD become more popular to be explored in several other chemical production and reactions. In several systems such as methyl acetate system serves as a model esterification system in a reactive distillation (Steigeneweget al., 2001). To generate the experimental data, RD pilot plant should be build first. However, to build a pilot plant, the feasibility and operating parameters need to be studied so that a suitable configuration can be proposed to build the RD column.

In fact, the previous study by (Steinigeweg & Gmehling, 2003) has done to determine the influence of important operating and design factor of reactive distillation for esterification of fatty acid decanoic acid with methanol to produce decanoic acid methyl esters. Simulations on RD need to be running in order to attain the result for feasibility and configuration for production of biodiesel. Therefore in, the use and design of RD is still developing to produce suitable RD and use less cost of production.

1.3 Objectives of Study

The specific objectives of this study are:

i. To propose a suitable configuration for reactive distillation
ii. To identify the important parameter that affect the process in reactive distillation

iii. To study feasibility of producing biodiesel, esterification of lauric acid and 2-ethylhexanol using super acidic sulfate zirconia catalyst in reactive distillation

1.4 Scope of studies

This study consists of three main scopes namely:

i. Setup base case RD using existed reactive reaction and using suitable thermodynamic model in the ASPEN Plus 12.1

ii. Find the important parameter of RD by changing the reflux ratio, feed location, pressure, height or reactive section and also the temperature of the reactant.

1.5 Rational and significant

Rationally, in this present study, simulation should be considered before setting up the biodiesel plant, this will cost of preventing from building not appropriate plant. The simulation study also can bring forward toward reducing the cost of building the plant. Significantly, the main purpose of this study can be archived by finding the important parameters that can be cooperating into RD column before building up the plant to produce biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Production of Biodiesel

Recent concern over diminishing fossil fuel supplies and the unsustainable price of oil, as well as adverse environmental and human health impact from the use of petroleum fuel have prompted considerable interest in research and development of fuel from renewable resources such as biodiesel. Biodiesel is a very attractive alternative fuel, as it is derive from a renewable, domestic resource and can, therefore, reduce reliance on foreign petroleum imports (Alex et al., 2007). Biodiesel reduces net carbon dioxide emissions by 78% on a life-cycle basis when compared to traditional diesel fuel (Tyson, 2001). In addition biodiesel is also been shown to have dramatic improvements on engine exhaust emission. For instance, combustion of neat biodiesel decreases carbon monoxide (CO) emission 46.7% , particulate matter emission by 66.7% and unburned hydrocarbons by 45.2% (Schumacher et al., 2001). Biodiesel also biodegradable and non-toxic, making it useful for transportation application in highly sensitive environments, such as marine ecosystem and mining enclosure.

Biodiesel is usually produced by the transesterification of a lipid feedstock. Transesterification are mainly performed using acid or base homogenous catalyst: sulfuric, sulfonic, phosphoric and hydrochloric acid as acid catalyst (Otera, 1993;

Corma, 1998) and alkaline hydroxide, metal alkoxide or acetates as based catalyst. However, the use of homogenous catalyst required neutralization and separation from the reaction mixture. As this matter occurs, heterogeneous catalyst is used instead of homogenous catalyst that leads to environmental problem. Furthermore, study on heterogeneously catalyzed transesterification for production of biodiesel industrial production by (Tanguy et al., 2006). In addition esterification of fatty acid is also a common practice in producing biodiesel and also in chemical industry. Because of this matter, the uses of reactive distillation (RD) currently develop for chemical and biodiesel production.

An experimental study have also been done using either in stirred batch reactor and also fixed bed-reactor to investigate the promising method esterification of free fatty acid (FFA) found in vegetable oil with methanol using solid catalyst to convert FFA into valuable fatty acid methyl ester (FAME) or biodiesel (Ni & Meunier, 2007). Kinetic behavior for the esterification of acetic acid with isoamyl alcohol in the temperature and molar feed ratios was investigated experimentally in a stirred batch reactor using Purolite C-175 calatlyst and resulting the equilibrium conversion of acetic acid was found to increase slightly with an increase in temperature and also it increases appreciably with an excess of isoamyl alcohol in the reacting system (Teo & Saha, 2004).

2.2 Reactive Distillation (RD) Column

2.2.1 Why RD?

The combination of reaction and distillation within one unit operation is called distillation column. RD has become interesting alternative to some conventional processes, especially for equilibrium-limited reaction as esterification and etherification. RD gives a direct removal of the product and intermediates results in higher conversion and selectivity compare to conventional processes. Conceptually, a RD column consists of there basic elements: rectifying section on the

top, reactive section in the middle and stripping section at the bottom (I-Kuan Lai et al., 2008). The reactive distillation is featured with its merits not only in promoting the reaction conversion, but also reducing both capital and operational cost as its multifunctional nature.

Since the RD process is first appeared in 1932 (Keyes, 1932) for production of ethyl acetate and lately become new focus in 1980's, since Eastman Chemical Company owned commercial RD process for production of methyl acetate. Later on, extensive researches on RD process appeared in the literature. At the same time, successful commercial processes that applied reactive distillation are installed for producing various chemicals such as methyl *tert*-butyl ether, (MTBE), cumene, ethyl-benzene and 3-methyl-1-butene, etc. In fact, practices of using RD for production methyl acetate and MTBE demonstrate its ability to render cost-effectiveness and compactness to chemical plant (Sharma & Mahajani, 2003).

Reactive distillation (RD) is widely used in many processes where a reversible reaction takes place (Malone and Doberty, 2000; Taylor and Krishna, 2000). RD process has shown great economical and environmental benefits in many existing applications (Jakobsson and Pyhalahti, 2002; Andreas and Franz, 2002; Wang and Shen, 2000; Kening et al., 2001), e.g., production of MTBE, methyl acetate, and so on. A comprehensive review article on RD has been published recently (Halpern, 2003). By using a solid super-acid catalysts fixed inside a catalytic zone of a distillation column, RD brings new possibilities of simplification to the ethyl lactate technology, making the process more environmental friendly compared with common homogeneous processes.In general, reactive distillation seems to be a simple, energy-saving process with lower investment and operation costs (Doherty and Buzad, 1992; Sundmacher and Homann, 1994).

2.2.2 Simulation of the RD Process

2.2.2.1 What is Process Simulation/Analysis?

The purpose of analysis/simulation is to model and predict the performance of a process. It involves the decomposition of the process into its constituent elements (units) for individual study of performance. The process characteristics (flowrates, compositions, temperatures, pressures, properties, equipment sizes, etc.) are predicted using analysis techniques. These techniques include mathematical models, empirical correlations and computer-aided process simulation tools (*ASPEN Plus*). In addition, process analysis may involve the use of experimental means to predict and validate performance. Therefore, in process simulation, we are given the process inputs and flowsheet and are required to predict process outputs (Fig. 2.2). The lab will focus on ASPEN Plus. It is a computer-aided software which uses the underlying physical relationships (e.g., material and energy balances, thermodynamic equilibrium, rate equations) to predict process performance (e.g., stream properties, operating conditions, and equipment sizes.

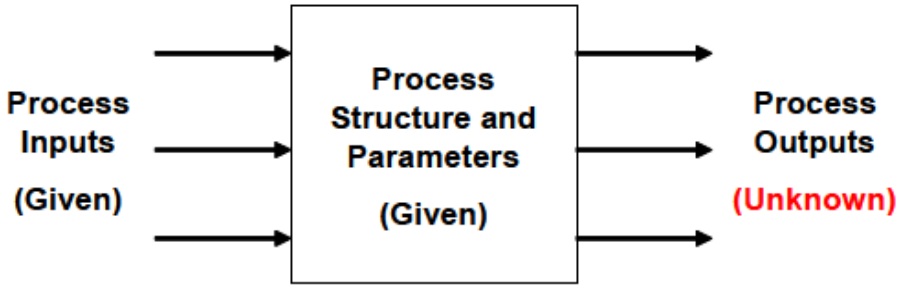

Figure 2.1 process simulation problems

2.2.2.2 Reactor Column

Usually, reactive distillation process requires several experimental data for the evaluation of its performance and deign. In order to reduce the experimental work, reliable and accurate process simulation tool can be used for obtaining useful information needed for the design (S. Bahtia et al., 2007). In the present study all simulation has been carried out using equilibrium stage model available in aspen plus

version 12.1 to simulate the process in reactive distillation column. Five parameters have been carried out to determine the important parameters that affect the process in RD distillation.

RADFRAC module is the steady state simulator Aspen Plus version 12.1 is based on rigorous equilibrium stage model for solving mass balance, phase equilibrium, summation and energy balance (MESH) equations. The equilibrium stage model assumes vapor liquid equilibrium at each stage. The departure from equilibrium is accounted at each stage for by tray efficiency or height equivalent to theoretical plate (HETP) (Bahtia et al., 2007). Besides that (Steinigeweg et al., 2003; Bhatia et al. 2007) practiced the used of RADFRAC module in RD column.

2.2.3 Phase equilibrium model

Vapor phase was assumed to be ideal and the UNIQUAC model was used to represent the activity coefficients in the rate expression. The UNIQUAC model has been reported to predict the non ideality in liquid phase satisfactorily for the esterification reaction system (Bhatia et al.,, 2006). The values of two activity-based kinetic parameters, was estimated from experimental data on initial reaction rates and liquid activity coefficients as assessed from UNIQUAC (Omota et al., 2003).

2.2.4 Reaction kinetics model

In process of 2-ethylhexanol and dodecanoic acid the reaction order was found to be linear regression by (Omota et al., 2003) using Eq (2.1), in logaritmatic form.

$$r_{0,u} = k_u C_{acid,0}^{n1} C_{alcohol,0}^{n2} \qquad \textbf{(2.1)}$$

First order regard to 2-ethylhexanol and catalyst concentration, respectively. Accordingly, the initial reaction rate r_0 is the sum of non-catalyzed and catalyzed rate:

$$r_{0,u} = k_u C_{acid,0}^2 C_{alcohol,0} + k_c C_{acid,0} C_{alcohol,0} C_{catalyst,0} \quad \textbf{(2.2)}$$

The initial reaction rates r_0 were estimated measurements of conversion versus time in temperature of 333 to 453 K. The rate constants k_u and k_c were calculated from initial reaction rates and initial concentration. All this information was gained by (Omota et al., 2003). The activation energies of esterification of 2-ethylhexanol and dodecanoate acid using sulfated zirconia and being plotted into graph of Arrhenius is 55.5kJ mol^{-1}. Concentration-based constant Eqn. (2.3), K_x already presented earlier (Omota, Dimian, & Bliek, 2003)

$$K_x = \frac{C_{ester}^{eq} C_{water}^{eq}}{C_{acid}^{eq} C_{alcohol}^{eq}} \quad \textbf{(2.3)}$$

Hence, the following expression can be formulated for the overall reaction rate which is consistent over whole concentration interval between zero and equilibrium as in Eqn (2.4).

$$r = \left(k_u C_{acid} + k_c C_{catalyst}\right)\left(C_{acid} C_{alcohol} - \frac{C_{ester} C_{water}}{K_x}\right) \quad \textbf{(2.4)}$$

The regressed values for concentration-based equilibrium constant for forward reaction were taken from (Omota et al., 2003). The values of K_x which varies for each temperature then used to find rate constant of backward reaction K_b using Arrhenius equation. Kinetic parameter need to be included to find the values of K_b are shown in the table 2.1